Applications of Lignin in Wood

Subjects: Materials Science, Paper & Wood Contributor: Johannes Karthäuser

Lignin is the most abundant aromatic polymer in nature and the second most abundant biomass on earth. In paper production and other processes, lignin is obtained as a side product and mainly used energetically. The use of lignin in wood adhesives or for wood modification has received a lot of scientific attention.

Keywords: lignin ; adhesive ; LPF resins

1. Composition of Lignin

The chemical structure of lignin varies significantly depending on the lignin source. Thus, upon considering lignin for any application, the characteristics of the different lignins have to be known, and the right type of lignin has to be carefully selected based on the target application.

Natural lignin is mainly built from three monomers, ρ -coumaryl alcohol (H-lignin unit), coniferyl alcohol (G-lignin unit) and sinapyl alcohol (S-lignin unit). The ratio between these monomers differs among lignins of different plant species and in different parts of the plants ^{[1][2]}. As such, the lignin in hardwood contains a higher quantity of S-lignin units, while softwood lignin contains more G-lignin units. H-lignin units are less abundant in wood, they can mainly be found in other plants ^{[3][4]}. The most common bond connecting the monomers in all natural lignins is the β -O-4 ether bond ^{[5][6]}. About 45–50% of the bonds in softwoods, and 60–62% in hardwoods are β -O-4 ether bonds ^[1].

For application in wood material treatment G- and H-lignin units and thus softwood or grass lignin is widely considered most promising. The reason for this can be found in the structure of the monomers; G- and H-lignin units have more reactive sites at the benzene ring, making them more reactive toward other binding material or chemical treatment ^{[3][4]}. Despite this, recent results have indicated that the lower molecular weight and other characteristics of hardwood lignin molecules might compensate for the lower number of reactive sites, thus producing lignin-phenol-formaldehyde (LPF) resins with similar characteristics. This topic is still under discussion, and a conclusion cannot be given ^{[Z][8][9]}.

Chemical extraction or treatment of lignin leads to even more variance between different lignins. In general, it was found that harsher treatment conditions lead to more significant changes of the structure, up to a point where the structure of these lignins, which are called technical lignins, does not have much in common with the structure of the naturally occurring lignin ^[1].

One of the most prominent examples of this is the Kraft process for production of chemical pulp. Due to high temperature and alkaline conditions, the structure of the lignin is dramatically changed during the process. The resulting Kraft lignin is a recalcitrant material, which is less reactive than natural lignin. Yet a lot of research on the usage of Kraft lignin has been carried out up to date ^{[1][10]}. However, there are also other important processes, during which lignin is extracted as a side product.

In the sulfide process, the lignocellulosic material is treated similarly to the Kraft process, but in an acidic medium. Lignins from the sulfide process are called lignosulfonates. They often have a higher molecular weight than Kraft lignin and are soluble in water due to the sulfonation at the α -position ^[11]. Due to the high amount of active sulfonic acid groups lignosulfonates are suitable for various potential applications such as dispersants or emulsifiers ^[12].

Soda pulping is a pulping procedure during which no sulfur is used. It is the main pulping method for non-wood species. The main difference between soda pulping lignin and Kraft lignin is the lower sulfur content ^{[13][11]}.

Because of the inert and recalcitrant structure of the aforementioned technical lignins, the "lignin-first" approach has received increasing attention. The idea of the approach is to cleave the lignin in a way that valuable products are gained. This could, for example, be achieved via solubilizing lignin with organic solvents ^[14]. Lignin that is cleaved from the

lignocellulosic materials and dissolved by organic solvents is known as organosolv lignin. Usually, organosolv lignin is closer in structure to natural lignin, compared to other technical lignins $\frac{11}{2}$. However, this largely depends on the severity of the extraction. The solvent also plays a significant role in the yield and composition of the product $\frac{15[16]}{2}$.

A more in-depth description on the different types and sources of lignin can be found elsewhere [11][17].

2. Applications of Lignin in Wood

Lignin is of interest for various applications in wood products. Most research has been carried out on the application of lignin as an adhesive. Adhesives are used for both solid wood and wood materials, as well as in engineered wood products such as fiberboards. For this application cleaving the lignin is not necessary because adhesives do not have to diffuse into the cell wall ^[18].

Cleaving the lignin is necessary for a different application, for which lignin-derived substances have high potential. Resins are commonly used for chemical wood modification. Chemical wood modification aims to improve important wood properties like dimensional stability, resistance to moisture, and bio-degradation, etc. To modify the wood, the modification material must enter the cell walls of the wood, and not just the wood lumen ^{[19][20]}. The cell walls can be entered from the lumen through micropores, which upon swelling have a maximum diameter of 2–4 nm in a water-saturated state ^[20]. Because of this diameter only smaller molecules can enter the cell walls ^{[21][22]}. As to be expected for a polymer, lignin molecules are too large for this. Because of this, lignin has to be cleaved for applications in chemical wood modification. Additional reasons for cleaving the lignin are the increase of reactive sites, a potential decrease of steric hindrance ^[23], as well as the potential production of other valuable chemicals, such as vanillin ^[24].

3. Applying Lignin without Cleavage

3.1. General Remarks

Considering the branched and stable structure of lignin, the most energy-efficient solution for applying lignin technically would be to apply it without cleavage. As mentioned before, lignin can be used without cleavage for adhesive applications.

Generally, lignin has a lower reactivity than monomers commercially used for resins. The reason for this is steric hindrance as well as additional substitutes on potential reactive sites and on the phenolic hydroxy group. The numbers of reactive sites for different lignins can, for example, be in the range of $0.81-1.72 \text{ mmol} \cdot \text{g}^{-1}$, depending on the lignin source ^[25]. This results in longer pressing times or higher temperatures needed for the curing of the resins containing higher amounts of lignin ^[26]. Due to this, methods for pretreatment of lignin to improve the reactivity of the lignin and thus the energy efficiency are necessary.

3.2. Application in PF Resins

PF resins can be classified into resole-type and novolac-type PF resins. Resoles are formed under alkaline conditions and in excess of formaldehyde, while novolacs are formed under acidic conditions and in excess of phenol. While there are some publications on substituting phenol in novolacs with lignin ^{[27][28][29]}, to the authors' knowledge, lignin-containing novolacs have not been applied in wood applications up to date.

3.2.1. Methylolated Lignin in Resoles

To improve the reactivity and thus the feasibility of lignin, various pretreatment methods are used ^{[13][23]}. An important method for pretreatment of lignin is methylolation. The aim of methylolation is to add functional hydroxymethyl groups to the lignin so that the lignin can directly react with the polymeric network of the resin. Herein, usually the reaction of formaldehyde with lignin under alkaline conditions is applied ^[23].

Kalami et al. (2017) managed to produce a resin made from methylolated lignin and formaldehyde, completely replacing the phenol. Timber joints produced with this adhesive exhibited shear lap strengths that were in accordance with the respective national requirements [30]. In a follow-up study, lignins from different sources were compared, showing that lignin containing more H- and G-lignin units are more suitable to replace phenol. The obtained resins performed only slightly worse than the PF resin, even with full replacement of phenol, while decreasing the formaldehyde consumption by up to 50% ^[4].

The formaldehyde emission of lignin-containing resins has to be examined with care in both PF and UF resins. Several publications reported higher formaldehyde emissions, due to the lower reactivity of the lignin compared to other monomers ^{[31][32][33]}, while others reported similar or even lower formaldehyde emissions ^{[34][35][36][37]} upon replacing part

of the phenol or urea monomers with lignin. This indicates that the formaldehyde emission is highly dependent on the ratio of monomers to formaldehyde, and on the reaction conditions.

Ghorbani et al. compared the influence of 20–40% of different types of technical lignins (organosolv, soda, Kraft and lignosulfonates) on PF resins. It was found that out of the given samples pine Kraft lignin and lignosulfonates were the most suitable lignins for replacing phenol. Beech veneer plywood produced with an LPF resin with 20–40% content of pine Kraft lignin even surpassed the tensile shear strength and wet tensile shear strength of PF resin. However, a higher curing temperature was applied to obtain these good properties ^{[3][38]}. In a follow-up study, LPF with 40% pine Kraft lignin was applied as an adhesive for beech plywood. The shear strength of the plywood was significantly lower than that of the PF, however, the plywood was suitable for exterior applications according to EN 314-1 ^[39]. Similarly, another publication reported that at 50% replacement of phenol by Kraft lignin the shear strength and especially the wet shear strength of plywood produced with LPF were inferior to those with PF resin ^[40]. These results were contradicted by another study, in which up to 50% Kraft lignin led to similar or even slightly improved performance compared to PF-bonded plywood ^[41]. Even higher substitution levels were reported by Abdelwahab et al. (2011), where up to 90% of phenol was substituted with Kraft lignin. The adhesives were tested according to ASTM D 2339-94A, and the adhesive strength was significantly higher for lignin-containing resins than for control PF resin, even at higher lignin concentrations ^[42].

In contrast to the results published by Ghorbani et al., Cheng et al. obtained very good results using organosolv lignin in a PF resin. Even at 75% replacement of phenol by organosolv lignin extracted from pine saw dust, the shear strength and the wet shear strength of plywood produced with the LPF resin were higher than those of a reference PF resin ^[43]. The high potential of organosolv lignin was confirmed in another study, where up to 70% replacement of phenol by the organosolv lignin "BioligninTM" by the company CIMV led to increased shear strengths compared to reference PF resin in plywood ^[44].

Eucalyptus plywood was produced with PF resin in which phenol was substituted with 5–25% enzymatic hydrolysis lignin from cornstalk residues from bio-ethanol production extracted with sodium hydroxide solution. The plywood almost met the requirements for first grade plywood according to the Chinese National Standard (GB/T 14732-2006). The best results were achieved with 10% phenol substitution ^[45]. Another study using enzymatic hydrolysis lignin indicated that in adhesives the substitution of up to 50% of the phenol is possible without inferior mechanical performance. A shear strength of 1.05 MPa was reported for three-layered plywood at 10% substitution of phenol with lignin ^[46]. A similar shear strength was reported for plywood made with a resin of 25% phenol, 25% urea and 50% unpurified bio-ethanol fermentation residues. Three-layer plywood bonded with this resin met the Chinese national standards according to GB/T 17657-1999 ^[42].

Another comparison between LPF made with different lignins indicated that alkaline-extracted lignin was most suitable out of alkaline-extracted, Kraft, organosolv and enzymatic hydrolysis lignin, at a substitution rate for 20% phenol. Particle boards produced with Kraft lignin containing LPF were suitable for P6 applications according to DIN EN 312:2010-12; the particle boards produced with enzymatic hydrolysis lignin, alkaline-extracted lignin and organosolv lignin containing LPFs performed well enough for P5 applications ^[9]. In another study on particle boards with PF resins, it was reported that 20–30% of the phenol could be substituted with organosolv lignin without a significant effect on the properties of the particle board ^[48].

In a comparison between lignin separated from different biomasses, including sugar mill bagasse, coconut coir, eucalyptus bark, and coffee beans using sodium hydroxide on small scale, each of the tested lignins improved the mechanical performance of wood samples bonded with PF resin up to 50% substitution tested according to IS 851:1978 [49].

3.2.2. Other Pretreatment Methods for Lignin in Resoles

Phenolation is the condensation of phenol and lignin, providing more reactive sites as well as cleavage of the ether bonds ^{[23][25]}. Plywood panels made with LPF with phenol substituted with 33% phenolated lignin and formaldehyde performed worse than plywood made with PF resin or plywood made with LPF resin with methylolated lignin ^[50].

The preparation of methylolated nanosized alkalilignin could be interesting for application in PF resins, since it can be done in mild conditions by acidic precipitation from ethylene glycol. Tests of the performance of plywood produced with nanolignin-PF resins indicated a higher bond strength and wet bond strength at similar or slightly lower formaldehyde emission compared to normal PF resins. The highest bond strengths and wet bond strengths were achieved at 30 and 40% substitution of phenol with nanolignin ^[35]. In another study 5 or 10% of nanosized and microsized alkali lignin was added to a PF resin, with the best properties being achieved with 5% nanolignin. The shear strength of wood lap joints with the resin could be increased from 8.7 MPa (pure PF resin) to 10.9 MPa ^[51].

The modification of the pine wood Kraft lignin by Fenton-oxidation and Fenton-oxidation with subsequent ammoxidation did not improve the performance of LPF resins as wood adhesives ^[52].

Substituting 30% of phenol with demethylated soda lignin in an LPF resin considerably decreased the performance of plywood produced with the resin. Only lignin demethylated with Na_2SO_3 could be promising for future applications ^[53].

3.2.3. Comparison of Selected Examples

For better comparison, selected examples of different PF resins, the wood sample and the mechanical properties measured for it are presented in <u>Table 1</u>.

Table 1. Resin composition, sample type, and mechanical properties of selected PF resins described in literature.

Phenol Substitution Levels in the Resin	Wood Sample	Mechanical Properties	Reference
20% substitution with methylolated organosolv lignin	Particle board	Internal bond strength (IB) = 1.02 MPa, Thickness swelling (TS) (2 h) = 10.6%	[48]
PF resin with 5% nanolignin	Wood lap joints	Shear strength = 10.9 MPa	[51]
100% substitution with methylolated enzymatic hydrolysis lignin	Plywood	Dry shear strength: 3.4 MPa (84% wood failure), wet shear strength: 2.6 MPa (73% wood failure)	[30]
40% phenolated sodium lignosulfonates	Plywood	Shear strength = 5.6 MPa	[38]
Lignin-Formaldehyde resins with methylolated softwood Kraft lignin, and corn stover enzymatic hydrolysislignin	Plywood	Enzymatic hydrolysis lignin: shear strength = 3.2 MPa (75% wood failure), softwood Kraft lignin: shear strength = 2.6 MPa (41% wood failure)	[<u>4</u>]
50% replacement with methylolated pine sawdust organosolv lignin	Plywood	Tensile strength = 2.25 MPa (93% wood failure), tensile wet strength = 1.9 MPa (85% wood failure)	[43]
PF resin with 30% nanolignin	Plywood	Dry bond strength = 1.59 MPa (100% wood failure), wet bond strength = 0.89 MPa (100% wood failure)	[35]

3.3. Application in UF Resins

Because of the similarity in structure, the application of lignin in PF resins is the first that comes to mind; however, lignin can also form bonds with other resins. The most prominent example of this is the formation of lignin-urea-formaldehyde (LUF) resins, because UF is the most produced adhesive for wood applications worldwide ^[54].

Addition of up to 20% of phenolated Kraft lignin only slightly decreased the internal bond strength of a UF resin in a particle board while significantly lowering the formaldehyde emission of the board ^[34].

Lignin can be pretreated with ionic liquids, which separates the lignin from lignocellulosic biomass. Treatment with ionic liquids decreases the quantity of methoxy-groups, thus increasing the reactivity of lignin ^[55]. Replacing urea in UF resins by soda bagasse black liquor treated with ionic liquids led to a decrease in shear strength and wood failure in plywood. The decrease in shear strength and wood failure was less pronounced than for samples with the same amount of untreated black liquor, confirming the increase of reactivity ^[56]. In a follow-up study, the performance of the LUF resins could be improved by the addition of 6% of the resin weight of polymeric diphenylmethane diisocyanate (PDMI). However, a direct comparison to UF resin was not described ^[57].

Another pretreatment method for the application of lignin in UF resins was recently presented by Gao et al. (2020) ^[36] for the application as an additive in plywood and medium-density fiberboards (MDFs). Methylolated lignin was esterified with maleic anhydride. The addition of 5% of maleic anhydride-treated lignin to a UF resin for plywood applications performed comparatively as well as plywood treated with reference UF resin while additionally decreasing the water absorption of the plywood ^[36].

The storage time of UF resin could be increased from 30 d to 200 d with addition of 20% methylolated sodium lignosulfonate. The formaldehyde emission and shear strength of eucalyptus plywood cured with the modified resin only slightly changed compared to pure UF resin. However, at 60% substitution, the properties were significantly worse ^[33].

For better comparison, selected examples of different UF resins, the wood sample and the mechanical properties measured for it are presented in <u>Table 2</u>.

Table 2. Resin composition, sample type, and mechanical properties of selected UF resins described in literature.

Urea Substitution Levels in the Resin	Wood Sample	Mechanical Properties	Reference
10% ionic liquid pretreated soda bagasse lignin	Plywood	shear strength = 1.89 MPa, wood failure = 70%	[56]
5% lignin-based polyacid catalyst	Plywood and MDF	Plywood: shear strength = 1.72 MPa, wet shear strength = 1.2 MPa MDF: IB = 1.35 MPa, 24h TS = 9%	[<u>36]</u>
15% ionic-liquid-treated soda bagasse lignin with 6% PMDI additive	Plywood	Dry shear strength = 2.2 MPa (100% wood failure), wet shear strength = 0.99 MPa (70% wood failure), water adsorption = 22%	[57]

3.4. Application in Other Resins

Glyoxal was used to synthesize a formaldehyde-free lignin-urea-glyoxal (LUG) resin. The mechanical properties and the water resistance of the LUG resin were worse than those of resins with formaldehyde; however, they could be improved by adding nanoclay or epoxy resin. The best results were achieved with 5% of the weight of the resin addition of epoxy resin. The wood failure in dry shear strength tests was 100% at 1.7 MPa, the wet shear strength was 1.3 MPa with 80% wood failure ^{[58][59]}. Additionally, research on the use of glyoxal in lignin-phenol-glyoxal (LPG) resin with black liquor from soda bagasse in particle boards was done. The particle boards performance was inferior to a reference PF resin; however, the requirements for the related EN-standards were still fulfilled ^[60]. In a follow-up study, the performance of the resin was improved by adding 7% of the resins' weight of epoxy resin. Plywood bonded with this resin had shear strength, wet shear strength and water absorption comparable to plywood produced with reference PF resin ^[61].

Another approach was proposed by Zhang et al. (2019) ^[62], who described a lignin-furfuryl-glyoxal adhesive. Adding up to 9% of the resins' weight of epoxy resin to improve the water resistance, the adhesive was used for beech wood particle boards. While the internal bond (IB) strength, the wet IB strength and the curing time of the particle boards were worse than with a commercial PF resin, they still met the Chinese regulation requirements according to GB/T17657(2006) ^[62].

A method to increase the water resistance of LPF resins is to add furfural. Resins made with 50% phenol replacement by Kraft lignin and 15% addition of furfural were used to produce plywood. The mechanical properties were similar to plywood produced with reference PF resin^[63].

Another field is the use of lignin in polyurethane adhesives. Lignin can improve the mechanical performance of polyurethanes when used as a polyol. Enhancing this effect even further can be achieved by using demethylated lignin. A total of 20% of polyethylenglycol in a polyurethane system with toluol-diisocyanate was replaced by the lignin. A tensile strength of 91.2 MPa was reported for the adhesives binding single aspen wood chips according to GB/T 9846-2015 ^[64]. A self-healing, recoverable polyurethane adhesive with 20% lignin modified with long chain polyetheramines was presented by Liu et al. (2020) ^[65]. The polyurethane adhesives all showed improved lap shear strengths upon addition of lignin or modified lignin, the best value being a lap shear strength of 7.8 MPa for beech wood boards in the first test (upon reusing, even higher values were achieved) ^[65].

Ammonium lignosulfonate treated with H_2O_2 and blended with polyethyleneimine was used as a binder in the production of MDF. Under optimal conditions (170 °C hot pressing temperature, 7 minutes pressing time, 20% binder content), the Chinese requirements for mechanical properties of MDF were met ^[66].

Other pretreatment methods and observations that were described in literature will be mentioned briefly below. Oxidation of lignin by laccase increases the reactivity ^[67]. Solvent fractioning can be used to obtain higher and lower molecular weight fractions from Kraft lignin. The results indicated that the mechanical properties of a cured LPF resin are not significantly influenced by the molecular weight of the lignin ^[68]. The reactivity of fractionated Kraft lignin can be improved by phenolation. However, plywood produced with an LPF resin with 40% phenolated Kraft lignin fractionated by solubilization in different solvents was inferior to plywood produced with PF resin for all fractions. Despite this, the properties of the plywood met the Chinese national standards GB/T14732 ^[31]. Lignin can function as a fire retardant and photo stabilizer in epoxy resins ^{[69][70]}.

Selected examples for different resins as well as their mechanical properties are listed in Table 3.

 Table 3. Resin composition, sample type, and mechanical properties of selected resins on different basis than PF and UF described in literature.

Resin Composition	Wood Sample	Mechanical Properties	Reference
LPG resin with 20% soda bagasse black liquor	Particle board	IB = 0.6 MPa, water absorption = 14%, thickness swelling = 10%	[60]
LPG resin with 30% bagasse soda black liquor and 7% epoxy resin	Plywood	Dry shear strength = 1.74 MPa (100% wood failure); wet shear strength = 1.0 MPa (80% wood failure), thickness swelling = 4%	[<u>61]</u>
LUG resin with 15% glyoxalated bagasse soda black liquor and 5% epoxy resin	Plywood	Dry shear strength = 1.7 MPa (100% wood failure), Wet shear strength = 1.3 MPa (80% wood failure), Water absorption = 6%	[59]
Polyurea adhesive doped with 20% polyetheramine chain grafted lignin with functional disulfide bonds	Beech wood boards	Lap shear strength = 7.8 MPa	[65]

References

- 1. Rinaldi, R.; Jastrzebski, R.; Clough, M.T.; Ralph, J.; Kennema, M.; Bruijnincx, P.C.A.; Weckhuysen, B.M. Paving the Wa y for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. Angew. Chem. Int. Ed. 2016, 5 5, 8164–8215.
- 2. Fengel, D.; Wegener, G. Wood: Chemistry, Ultrastructure, Reactions, Reprint der Orig.-Ausg. (ehem. de Gruyter); Kess el: Remagen, Germany, 2003; ISBN 978-3-935638-39-5.
- Ghorbani, M.; Liebner, F.; Van Herwijnen, H.W.G.; Pfungen, L.; Krahofer, M.; Budjav, E.; Konnerth, J. Lignin Phenol For maldehyde Resoles: The Impact of Lignin Type on Adhesive Properties. Bioresources 2016, 11, 6727–6741.
- Kalami, S.; Chen, N.; Borazjani, H.; Nejad, M. Comparative Analysis of Different Lignins as Phenol Replacement in Phe nolic Adhesive Formulations. Ind. Crop. Prod. 2018, 125, 520–528.
- 5. Chakar, F.S.; Ragauskas, A.J. Review of Current and Future Softwood Kraft Lignin Process Chemistry. Ind. Crop. Prod. 2004, 20, 131–141.
- 6. Wang, Y.; Wang, Q.; He, J.; Zhang, Y. Highly Effective C–C Bond Cleavage of Lignin Model Compounds. Green Chem. 2017, 19, 3135–3141.
- Lourençon, T.V.; Alakurtti, S.; Virtanen, T.; Jääskeläinen, A.-S.; Liitiä, T.; Hughes, M.; Magalhães, W.L.E.; Muniz, G.I.B.; Tamminen, T. Phenol-Formaldehyde Resins with Suitable Bonding Strength Synthesized from "Less-Reactive" Hardwo od Lignin Fractions. Holzforschung 2020, 74, 175–183.
- 8. Balakshin, M.; Capanema, E. Rethinking Biorefinery Lignins: Breaking Dogmas. In Proceedings of the 14th European Workshop on Lignocellulosics and Pulp; Grenoble INP, Autrans, France, 28 June–1 July 2016.
- 9. Stücker, A.; Schütt, F.; Saake, B.; Lehnen, R. Lignins from Enzymatic Hydrolysis and Alkaline Extraction of Steam Refin ed Poplar Wood: Utilization in Lignin-Phenol-Formaldehyde Resins. Ind. Crop. Prod. 2016, 85, 300–308.
- Crestini, C.; Lange, H.; Sette, M.; Argyropoulos, D.S. On the Structure of Softwood Kraft Lignin. Green Chem. 2017, 1 9, 4104–4121.
- 11. Kai, D.; Tan, M.J.; Chee, P.L.; Chua, Y.K.; Yap, Y.L.; Loh, X.J. Towards Lignin-Based Functional Materials in a Sustaina ble World. Green Chem. 2016, 18, 1175–1200.
- 12. Vishtal, A.; Kraslawski, A. Challenges in Industrial Applications of Technical Lignins. Bioresources 2011, 6, 3547–3568.
- 13. Wang, Y.-Y.; Meng, X.; Pu, Y.J.; Ragauskas, A. Recent Advances in the Application of Functionalized Lignin in Value-Ad ded Polymeric Materials. Polymers 2020, 12, 2277.
- 14. Paone, E.; Tabanelli, T.; Mauriello, F. The Rise of Lignin Biorefinery. Curr. Opin. Green Sustain. Chem. 2020, 24, 1-6.
- 15. Luo, H.; Abu-Omar, M.M. Lignin Extraction and Catalytic Upgrading from Genetically Modified Poplar. Green Chem. 20 18, 20, 745–753.
- Jiménez-López, L. Co-Production of Soluble Sugars and Lignin from Short Rotation White Poplar and Black Locust Cro ps. Wood Sci. Technol. 2020, 27, 1617–1643.
- 17. Liao, J.J.; Latif, N.H.A.; Trache, D.; Brosse, N.; Hussin, M.H. Current Advancement on the Isolation, Characterization a nd Application of Lignin. Int. J. Biol. Macromol. 2020, 162, 985–1024.

- Rowell, R.M. Handbook of Wood Chemistry and Wood Composites; CRC Press: Boca Raton, FL, USA, 2005; ISBN 97 8-0-8493-1588-6.
- 19. Bicke, S.; Militz, H. Modification of Beech Veneers with Low Molecular Weight Phenol Formaldehyde for the Production of Plywood: Comparison of the Submersion and Vacuum Impregnation; Laboratório Nacional Deengenharia Civil: Lisbo n, Portugal, 2014.
- 20. Hill, C.A.S. Wood Modification: Chemical, Thermal and Other Processes; Wiley Series in Renewable Resources; John Wiley & Sons: Chichester, UK; Hoboken, NJ, USA, 2006; ISBN 978-0-470-02172-9.
- Furuno, T.; Imamura, Y.; Kajita, H. The Modification of Wood by Treatment with Low Molecular Weight Phenol-Formalde hyde Resin: A Properties Enhancement with Neutralized Phenolic-Resin and Resin Penetration into Wood Cell Walls. Wood Sci. Technol. 2004, 37, 349–361.
- 22. Biziks, V.; Bicke, S.; Militz, H. Penetration Depth of Phenol-Formaldehyde (PF) Resin into Beech Wood Studied by Ligh t Microscopy. Wood Sci. Technol. 2019, 53, 165–176.
- 23. Hu, L.; Pan, H.; Zhou, Y.; Zhang, M. Methods to Improve Lignin's Reactivity as a Phenol Substitute and as Replacemen t for Other Phenolic Compounds: A Brief Review. Bioresources 2011, 6, 3515–3525.
- De Wild, P.J.; Huijgen, W.J.J.; Gosselink, R.J.A. Lignin Pyrolysis for Profitable Lignocellulosic Biorefineries. Biofuels Bio prod. Bioref. 2014, 8, 645–657.
- 25. Yang, S.; Wen, J.-L.; Yuan, T.-Q.; Sun, R.-C. Characterization and Phenolation of Biorefinery Technical Lignins for Ligni n–Phenol–Formaldehyde Resin Adhesive Synthesis. RSC Adv. 2014, 4, 57996–58004.
- 26. Klašnja, B.; Kopitović, S. Lignin-Phenol-Formaldehyde Resins as Adhesives in the Production of Plywood. Holz Roh. W erkst. 1992, 50, 282–285.
- Tejado, A.; Kortaberria, G.; Peña, C.; Labidi, J.; Echeverría, J.M.; Mondragon, I. Lignins for Phenol Replacement in Nov olac-Type Phenolic Formulations, Part I: Lignophenolic Resins Synthesis and Characterization. J. Appl. Polym. Sci. 200 7, 106, 2313–2319.
- Tejado, A.; Kortaberria, G.; Peña, C.; Blanco, M.; Labidi, J.; Echeverría, J.M.; Mondragon, I. Lignins for Phenol Replace ment in Novolac-Type Phenolic Formulations. II. Flexural and Compressive Mechanical Properties. J. Appl. Polym. Sci. 2008, 107, 159–165.
- 29. Jing, Z.; Lihong, H.; Bingchuan, L.; Caiying, B.; Puyou, J.; Yonghong, Z. Preparation and Characterization of Novolac P henol–Formaldehyde Resins with Enzymatic Hydrolysis Lignin. J. Taiwan Inst. Chem. Eng. 2015, 54, 178–182.
- Kalami, S.; Arefmanesh, M.; Master, E.; Nejad, M. Replacing 100% of Phenol in Phenolic Adhesive Formulations with Li gnin. J. Appl. Polym. Sci. 2017, 134, 45124.
- 31. Luo, B.; Jia, Z.; Jiang, H.; Wang, S.; Min, D. Improving the Reactivity of Sugarcane Bagasse Kraft Lignin by a Combinat ion of Fractionation and Phenolation for Phenol–Formaldehyde Adhesive Applications. Polymers 2020, 12, 1825.
- 32. Lee, W.-J.; Chang, K.-C.; Tseng, I.-M. Properties of Phenol-Formaldehyde Resins Prepared from Phenol-Liquefied Lign in. J. Appl. Polym. Sci. 2011.
- 33. Gao, S.; Cheng, Z.; Zhou, X.; Liu, Y.; Chen, R.; Wang, J.; Wang, C.; Chu, F.; Xu, F.; Zhang, D. Unexpected Role of Amp hiphilic Lignosulfonate to Improve the Storage Stability of Urea Formaldehyde Resin and Its Application as Adhesives. I nt. J. Biol. Macromol. 2020, 161, 755–762.
- 34. Younesi-Kordkheili, H.; Pizzi, A.; Niyatzade, G. Reduction of Formaldehyde Emission from Particleboard by Phenolated Kraft Lignin. J. Adhes. 2016, 92, 485–497.
- 35. Chen, Y.; Gong, X.; Yang, G.; Li, Q.; Zhou, N. Preparation and Characterization of a Nanolignin Phenol Formaldehyde Resin by Replacing Phenol Partially with Lignin Nanoparticles. RSC Adv. 2019, 9, 29255–29262.
- Gao, S.; Liu, Y.; Wang, C.; Chu, F.; Xu, F.; Zhang, D. Synthesis of Lignin-Based Polyacid Catalyst and Its Utilization to I mprove Water Resistance of Urea–Formaldehyde Resins. Polymers 2020, 12, 175.
- 37. Yang, S.; Wu, J.-Q.; Zhang, Y.; Yuan, T.-Q.; Sun, R.-C. Preparation of Lignin-Phenol-Formaldehyde Resin Adhesive Ba sed on Active Sites of Technical Lignin. J. Biobased Mat. Bioenergy 2015, 9, 266–272.
- Ghorbani, M.; Konnerth, J.; van Herwijnen, H.W.G.; Zinovyev, G.; Budjav, E.; Requejo Silva, A.; Liebner, F. Commercial Lignosulfonates from Different Sulfite Processes as Partial Phenol Replacement in PF Resole Resins. J. Appl. Polym. Sci. 2018, 135, 45893.
- 39. Ghorbani, M.; Liebner, F.; van Herwijnen, H.W.G.; Solt, P.; Konnerth, J. Ligneous Resole Adhesives for Exterior-Grade Plywood. Eur. J. Wood Prod. 2018, 76, 251–258.
- 40. Solt, P.; van Herwijnen, H.W.G.; Konnerth, J. Thermoplastic and Moisture-dependent Behavior of Lignin Phenol Formal dehyde Resins. J. Appl. Polym. Sci. 2019, 136, 48011.

- Kouisni, L.; Fang, Y.; Paleologou, M.; Ahvazi, B.; Hawari, J.; Zhang, Y.; Wang, X.-M. Kraft Lignin Recovery and Its Use i n the Preparation of Lignin-Based Phenol Formaldehyde Resins for Plywood. Cellul. Chem. Technol. 2011, 45, 515–52
 0.
- 42. Abdelwahab, N.A.; Nassar, M.A. Preparation, Optimisation and Characterisation of Lignin Phenol Formaldehyde Resin as Wood Adhesive. Pigment Resin Technol. 2011, 40, 169–174.
- 43. Cheng, S.; Yuan, Z.; Leitch, M.; Anderson, M.; Xu, C.C. Highly Efficient Depolymerization of Organosolv Lignin Using a Catalytic Hydrothermal Process and Production of Phenolic Resins/Adhesives with the Depolymerized Lignin as a Sub stitute for Phenol at a High Substitution Ratio. Ind. Crop. Prod. 2013, 44, 315–322.
- 44. Tachon, N.; Benjelloun-Mlayah, B.; Delmas, M. Organosolv Wheat Straw Lignin as a Phenol Substitute for Green Phen olic Resins. Bioresources 2016, 11, 5797–5815.
- 45. Jin, Y.; Cheng, X.; Zheng, Z. Preparation and Characterization of Phenol–Formaldehyde Adhesives Modified with Enzy matic Hydrolysis Lignin. Bioresour. Technol. 2010, 101, 2046–2048.
- 46. Qiao, W.; Li, S.; Guo, G.; Han, S.; Ren, S.; Ma, Y. Synthesis and Characterization of Phenol-Formaldehyde Resin Usin g Enzymatic Hydrolysis Lignin. J. Ind. Eng. Chem. 2015, 21, 1417–1422.
- 47. Pang, B.; Cao, X.-F.; Sun, S.-N.; Wang, X.-L.; Wen, J.-L.; Lam, S.S.; Yuan, T.-Q.; Sun, R.-C. The Direct Transformation of Bioethanol Fermentation Residues for Production of High-Quality Resins. Green Chem. 2020, 22, 439–447.
- 48. Cetin, N.S.; Ozmen, N. Use of Organosolv Lignin in Phenol-Formaldehyde Resins for Particleboard Production—I. Org anosolv Lignin Modified Resins. Int. J. Adhes. Adhes. 2002, 22, 477–480.
- 49. Khan, M.A.; Ashraf, S.M. Studies on Thermal Characterization of Lignin. J. Therm. Anal. Calorim. 2007, 89, 993–1000.
- 50. Vázquez, G.; González, J.; Freire, S.; Antorrena, G. Effect of Chemical Modification of Lignin on the Gluebond Perform ance of Lignin-Phenolic Resins. Bioresour. Technol. 1997, 60, 191–198.
- 51. Yang, W.; Rallini, M.; Natali, M.; Kenny, J.; Ma, P.; Dong, W.; Torre, L.; Puglia, D. Preparation and Properties of Adhesiv es Based on Phenolic Resin Containing Lignin Micro and Nanoparticles: A Comparative Study. Mater. Des. 2019, 161, 55–63.
- 52. Ghorbani, M.; Konnerth, J.; Budjav, E.; Silva, A.; Zinovyev, G.; van Herwijnen, H.; Edler, M.; Griesser, T.; Liebner, F. Am moxidized Fenton-Activated Pine Kraft Lignin Accelerates Synthesis and Curing of Resole Resins. Polymers 2017, 9, 4 3.
- 53. Li, J.; Wang, W.; Zhang, S.; Gao, Q.; Zhang, W.; Li, J. Preparation and Characterization of Lignin Demethylated at Atm ospheric Pressure and Its Application in Fast Curing Biobased Phenolic Resins. RSC Adv. 2016, 6, 67435–67443.
- 54. Younesi-Kordkheili, H.; Pizzi, A. A Comparison between Lignin Modified by Ionic Liquids and Glyoxalated Lignin as Mod ifiers of Urea-Formaldehyde Resin. J. Adhes. 2017, 93, 1120–1130.
- 55. Qu, Y.; Luo, H.; Li, H.; Xu, J. Comparison on Structural Modification of Industrial Lignin by Wet Ball Milling and Ionic Liq uid Pretreatment. Biotechnol. Rep. 2015, 6, 1–7.
- 56. Younesi-Kordkheili, H.; Pizzi, A.; Honarbakhsh-Raouf, A.; Nemati, F. The Effect of Soda Bagasse Lignin Modified by Ion ic Liquids on Properties of the Urea–Formaldehyde Resin as a Wood Adhesive. J. Adhes. 2017, 93, 914–925.
- 57. Younesi-Kordkheili, H.; Pizzi, A.; Mohammadghasemipour, A. Improving the Properties of Ionic Liquid-Treated Lignin-Ur ea-Formaldehyde Resins by a Small Addition of Isocyanate for Wood Adhesive. J. Adhes. 2018, 94, 406–419.
- 58. Younesi-Kordkheili, H. Improving Physical and Mechanical Properties of New Lignin-Urea-Glyoxal Resin by Nanoclay. Eur. J. Wood Prod. 2017, 75, 885–891.
- 59. Younesi-Kordkheili, H.; Pizzi, A. Improving the Properties of Urea-Lignin-Glyoxal Resin as a Wood Adhesive by Small A ddition of Epoxy. Int. J. Adhes. Adhes. 2020, 102, 102681.
- 60. Younesi-Kordkheili, H.; Pizzi, A. Some of Physical and Mechanical Properties of Particleboard Panels Bonded with Phe nol-Lignin-Glyoxal Resin. J. Adhes. 2020, 96, 1385–1395.
- 61. Younesi-Kordkheili, H.Y.; Pizzi, A. Improving Properties of Phenol-Lignin-Glyoxal Resin as a Wood Adhesive by an Epo xy Resin. Eur. J. Wood Prod. 2021, 79, 199–205.
- 62. Zhang, J.; Wang, W.; Zhou, X.; Liang, J.; Du, G.; Wu, Z. Lignin-Based Adhesive Crosslinked by Furfuryl Alcohol–Glyoxa I and Epoxy Resins. Nord. Pulp. Pap. Res. J. 2019, 34, 228–238.
- 63. Zhang, Y.; Li, N.; Chen, Z.; Ding, C.; Zheng, Q.; Xu, J.; Meng, Q. Synthesis of High-Water-Resistance Lignin-Phenol Re sin Adhesive with Furfural as a Crosslinking Agent. Polymers 2020, 12, 2805.
- 64. Chen, Y.; Fu, S.; Zhang, H. Signally Improvement of Polyurethane Adhesive with Hydroxy-Enriched Lignin from Bagass e. Colloids Surf. A Physicochem. Eng. Asp. 2020, 585, 124164.

- 65. Liu, W.; Fang, C.; Chen, F.; Qiu, X. Strong, Reusable, and Self-Healing Lignin-Containing Polyurea Adhesives. ChemS usChem 2020, 13.
- 66. Yuan, Y.; Guo, M.H.; Liu, F.Y. Preparation and Evaluation of Green Composites Using Modified Ammonium Lignosulfon ate and Polyethylenimine as a Binder. Bioresources 2013, 9, 836–848.
- 67. Raj, A.; Devendra, L.P.; Sukumaran, R.K. Comparative Evaluation of Laccase Mediated Oxidized and Unoxidized Ligni n of Sugarcane Bagasse for the Synthesis of Lignin-Based Formaldehyde Resin. Ind. Crop. Prod. 2020, 150, 112385.
- 68. Solt, P.; Jaaskelainen, A.-S.; Lingenfelter, P.; Konnerth, J. Impact of Molecular Weight of Kraft Lignin on Adhesive Perfo rmance of Lignin-Based Phenol-Formaldehyde Resins. For. Prod. J. 2018, 68, 7.
- 69. Marciano, S.J.; Avelino, F.; da Silva, L.R.R.; Mazzetto, S.E.; Lomonaco, D. Microwave-Assisted Phosphorylation of Org anosolv Lignin: New Bio-Additives for Improvement of Epoxy Resins Performance. Biomass Conv. Bioref. 2020.
- 70. Liang, X.; Hu, Q.; Wang, X.; Li, L.; Dong, Y.; Sun, C.; Hu, C.; Gu, X. Thermal Kinetics of a Lignin-Based Flame Retarda nt. Polymers 2020, 12, 2123.

Retrieved from https://encyclopedia.pub/entry/history/show/23830